

# Supercooled Water: Dynamics, Structure and Thermodynamics

Francis W. Starr<sup>1,4</sup>, Srikanth Sastry<sup>2</sup> \*, Francesco Sciortino<sup>3</sup> and H. E. Stanley<sup>4</sup>

<sup>1</sup> *Center for Theoretical and Computational Materials Science and Polymers Division, National Institute of Standards and Technology, Gaithersburg, Maryland 20899, USA*

<sup>2</sup> *Jawaharlal Nehru Centre for Advanced Scientific Research, Jakkur Campus, Bangalore 560064, INDIA*

<sup>3</sup> *Dipartimento di Fisica and Istituto Nazionale per la Fisica della Materia, Università di Roma La Sapienza, P.le Aldo Moro 2, I-00185, Roma, ITALY*

<sup>4</sup> *Center for Polymer Studies and Department of Physics, Boston University, Boston MA 02215, USA*

The anomalous properties of water in the supercooled state are numerous and well-known. Particularly striking are the strong changes in dynamic properties that appear to display divergences at temperatures close to – but beyond – the lowest temperatures attainable either experimentally or in computer simulations. Recent work on slow or glassy dynamics in water suggests analogies with simple liquids not previously appreciated, and at the same time highlights some aspects that remain peculiar to water. A comparison of the behavior of water with normal liquids, with respect to its dynamic, thermodynamic and structural changes in the supercooled regime is made by analyzing, via computer simulations, the properties of local potential energy minima sampled by water in supercooled temperatures and pressures.

## I. INTRODUCTION

Water is among the most abundant substances on earth, and also among the most familiar, as it forms a significant part of the natural environment, and of living organisms. In addition to these obvious reasons, the continued study of water by physical scientists stems from the many remarkable and peculiar properties it possesses, some of which are part of the popular lore (such as the fact that liquid water is heavier than ice near ambient conditions). In the crystalline state, water exists in as many as twelve, possibly fourteen, forms of ice. Echoes of this *polymorphism* are to be found in the *amorphous* state as well. When prepared as an *amorphous* solid, or glass, by ultrafast cooling or by depositing vapor on a cold substrate, water is found in two forms, a high density and a low density form [1].

A substantial fraction of the study of liquid water has focussed on its properties in the supercooled state [2], where its unusual properties are amplified. Analyzing a range of dynamic and thermodynamic quantities, Speedy and Angell [3] showed that these quantities appeared to diverge at a finite temperature in a power law fashion, leading to the hypothesis of a thermodynamic singularity at  $T_s = 228K$ . Computer simulation studies and analysis of simplified models have in recent years led to the proposal of two other possibilities, namely the existence of a liquid-liquid critical point at low temperatures [4], and the scenario wherein no thermodynamic singularities need be invoked to explain the anomalies observed in water [5].

However, there has been a renewed focus recently on the idea that regardless of a thermodynamic singularity, strong changes in both the thermodynamic and dynamic

properties of supercooled water may be expected in the vicinity of  $T_s$  [6–8]. Evidence from computer simulations suggests that the strong temperature dependence of dynamical quantities, and the power law temperature dependence, may be explained as manifestations of an avoided dynamical singularity described by the mode coupling theory of the glass transition [6]. Analysis of experimental data [7,8] appears to indicate that the rapid changes in the entropy of supercooled water must cross over to slower changes in the vicinity of  $T_s$ , and correspondingly, the heat capacity must display a maximum. It has been argued [7,8] that upon crossing this temperature, water changes character from being a very “fragile” liquid at higher temperatures, to a “strong” liquid at lower temperatures [9]. Specifically, the stronger than Arrhenius temperature dependence of relaxation times seen at temperatures higher than  $T_s$  is argued to cross over to Arrhenius dependence at lower temperatures (the experimental situation is ambiguous at present, with measurements in Ref. [11] arguing in favor of continuous change down to the glass transition temperature  $\sim 135K$ ).

Among the crucial issues one must address in understanding the above possibilities is the nature of structural change that takes place as liquid water is supercooled. In particular, the nature of structural change that accompanies a fragile to strong crossover must be understood. In this paper we present a preliminary report of investigations to address these questions, which focus on analyzing the properties of local potential energy minima or “inherent structures” sampled by a simulation model of water. Similar investigations have recently proved a fruitful approach to studying changes in liquid state properties under supercooling of model atomic liquids as well as liquid

water [12–17]. In particular, we focus on the comparison of changes in dynamics with changes in the energies of the inherent structures sampled, and structural change as evidenced by changes in the nearest neighbor geometrical properties. A specific structural feature we consider is the fraction of water molecules that are four-coordinated and those with five or greater other molecules in their first neighbor shell. These latter “bifurcated bond” arrangements have previously been shown to facilitate structural rearrangement and hence faster dynamics [10].

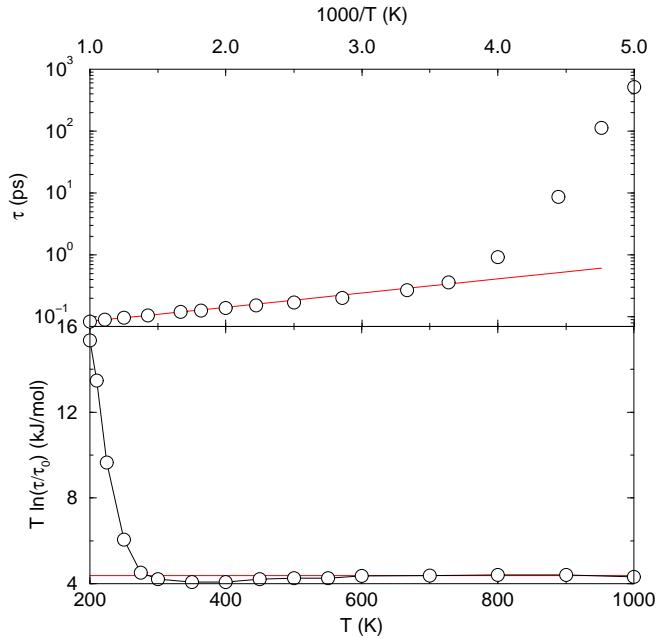


FIG. 1. Relaxation times: (a) Shown on a logarithmic scale *vs.* inverse temperature (Arrhenius plot). Deviations from Arrhenius behavior is observed at low temperatures. (b) Transformed to yield a constant value if Arrhenius behavior is obeyed.

## II. SIMULATION DETAILS

We perform molecular dynamics (MD) simulations of 216 water molecules interacting via the SPC/E pair potential [18]. The simulations we describe here are for a fixed density of  $\rho = 1.0 \text{ g/cm}^3$ , for temperatures ranging from  $210 \text{ K}$  to  $700 \text{ K}$ . For  $T \leq 300 \text{ K}$ , we simulate two independent systems to improve statistics, as the long relaxation times make time averaging more difficult. Full details of the simulation protocol used are described in [19]. At the studied density, the mode coupling singular temperature,  $T_c$  has been estimated to be  $T_c = 194 \text{ K} \pm 1$  [19].

Inherent structures are obtained, with a sample of 100 equilibrated liquid configurations as starting configurations, by performing a local minimization of the potential energy, using conjugate gradient minimization. The iterative procedure for minimizing the energy is performed until changes in potential energy per iteration are no

more than  $10^{-15} \text{ kJ/mol}$ . A normal mode analysis confirms that the potential energy changes with positive curvature along all directions away from the minimum energy configurations so obtained.

We calculate the oxygen-oxygen pair correlation function for both the equilibrium liquid configurations, and the inherent structures. The integrated intensity under the first peak of the pair correlation function (upto the cutoff radius  $0.31 \text{ nm}$ ) yields the coordination number. Dynamics is probed by calculating the self intermediate scattering function at wavevector  $18.55 \text{ nm}^{-1}$ , *i.e.* the Fourier transform of the self van Hove self correlation function

$$G_s(r, t) = \frac{1}{N} \sum_{i=1}^N \langle \delta(|\mathbf{r}_i(t) - \mathbf{r}(0)| - r) \rangle. \quad (1)$$

Stretched exponential fits of the self intermediate scattering function yield relaxation times  $\tau$  as a function of temperature. Average values of the inherent structure potential energy and pressure are also calculated.

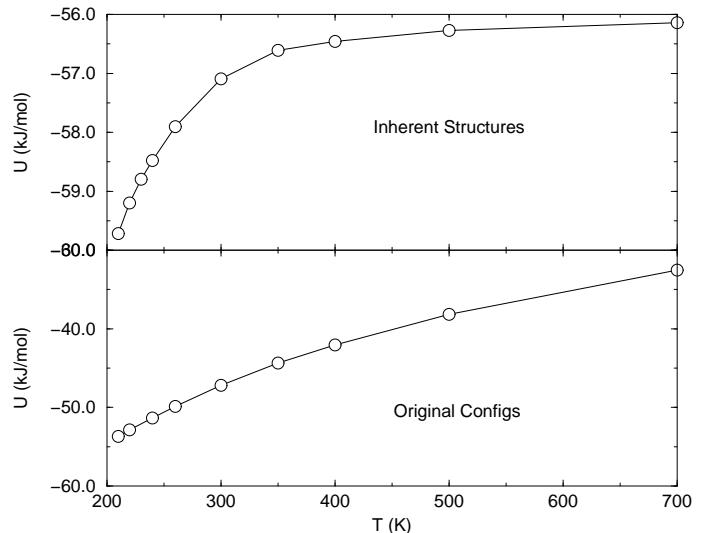


FIG. 2. (a) Average inherent structure energies. (b) Equilibrium averaged potential energies.

## III. RESULTS

Figure 1(a) shows the relaxation times plotted on a logarithmic scale against inverse temperature. Clear deviations from the high temperature Arrhenius behavior,

$$\tau = \tau_0 \exp(-E/k_B T) \quad (2)$$

(where  $E$  is a constant) is observed for  $T \lesssim 275 \text{ K}$ . This is more clearly seen by plotting  $T \ln(\tau/\tau_0)$  (where  $\tau_0$  is obtained from an Arrhenius fit of the highest 5 temperatures), as shown in Fig. 1(b), which shows strong deviation of  $T \ln(\tau/\tau_0)$  below  $T \sim 275 \text{ K}$  indicating that the

temperature dependence of relaxation times at low temperatures can no longer be described by the Arrhenius form.

Figure 2 (a) shows the average inherent structure energies as a function of temperature. For comparison, the equilibrium potential energy is shown in Figure 2(b). Inherent structure energies change continuously, with modest temperature dependence at high temperatures to substantial temperature dependence at lower temperatures. In particular, in the range of temperatures where the relaxation times begin to display non-Arrhenius behavior, the inherent structure energies show considerable temperature dependence. This behavior is analogous to that found for a model atomic fluid [12].

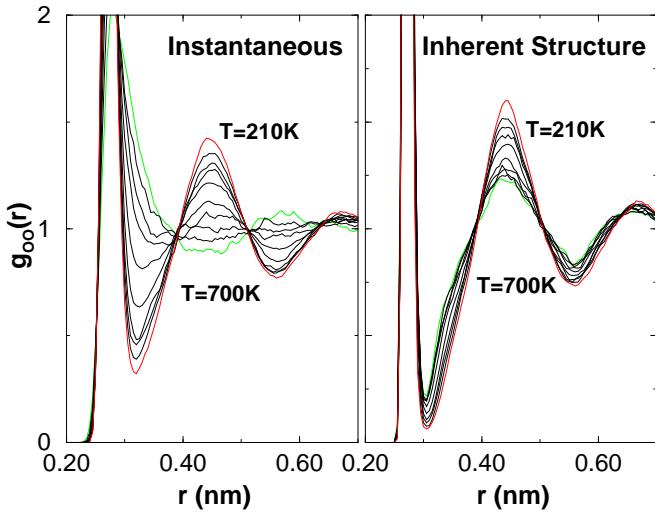


FIG. 3. Oxygen-oxygen pair correlation function, for (a) equilibrated liquid configurations, and (b) inherent structures. Upon lowering temperature, the first peak in both cases becomes sharper, and the intensity between the first and second peaks decreases. The smaller changes seen in the case of the inherent structures offers an estimate of that part of the change due to configurational change upon cooling, as opposed to thermal effects.

Figure 3 shows the oxygen-oxygen pair correlation function, (a) for the equilibrated liquid and (b) for the inherent structures. In contrast to the model atomic liquid studied in [12,13], both pair correlation functions show marked temperature dependence, at fixed density. In both Fig.s 3(a) and 3(b), the first peak of the pair correlation function becomes sharper upon decreasing the temperature. Further, there is a systematic reduction of the intensity between the first and second neighbor peaks. The integrated intensity under the first peak, which gives the average number of neighbor molecules in the first coordinate shell, approaches the value of 4 from higher values, as the temperature decreases. This implies that the configurations sampled by the liquid come closer to that of a four-coordinated random network.

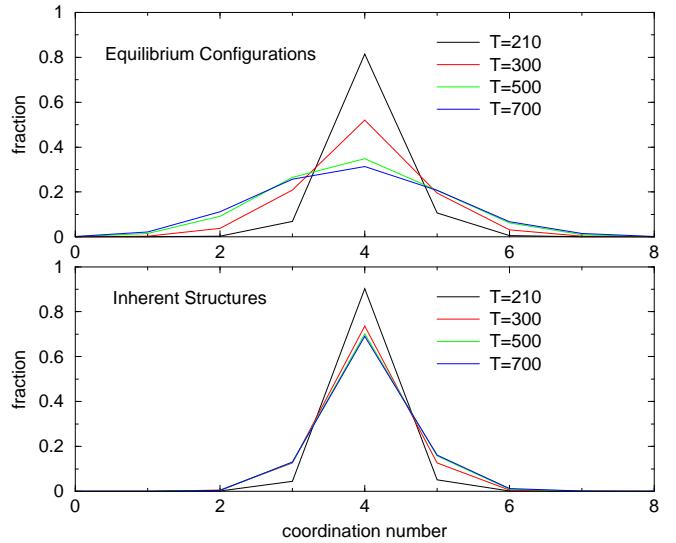


FIG. 4. Distribution of the coordination number of molecules: (a) Equilibrated configurations, and (b) Inherent structures. In both cases, the distribution becomes more narrowly distributed around four-coordination.

To quantify this further, Fig. 4 shows the histogram of the fraction of molecules with a given coordination number. For equilibrated configurations, the histogram changes from a rather broad one to one that is peaked around the value 4 as the temperature decreases. The same trend is visible for the inherent structures, although even at high temperatures, the distribution is quite narrowly peaked around the value 4. Such a comparison permits us to make a separation between deviations from four-coordination arising from thermal agitation [20], and that arising from configurational change.

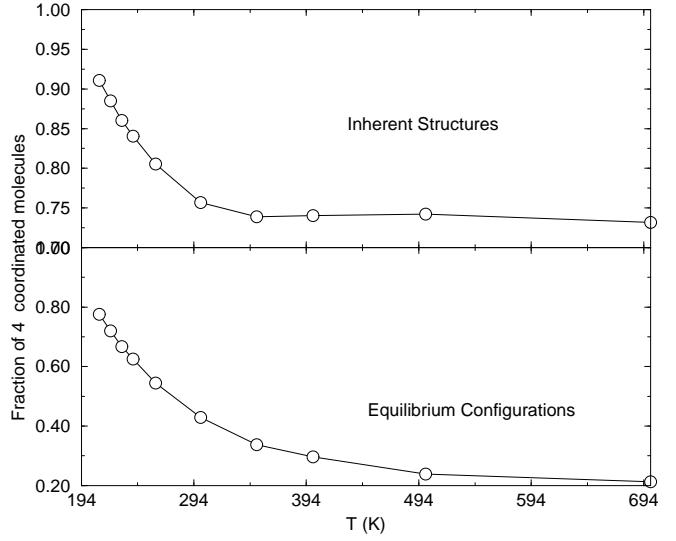


FIG. 5. Fraction of four coordinated water molecules: (a) Equilibrated configurations, and (b) Inherent structures

From data in Fig. 3 and 4, we calculate the fraction of molecules that are four-coordinated, and those that

have five or higher coordination, *i. e.* which have bifurcated bonds. Fig. 5 shows the temperature dependence of the fraction of four-coordinated water molecules. For both the equilibrated configurations and inherent structures, this fraction approaches *one* as  $T \rightarrow T_c$ . As with deviations from Arrhenius behavior, the range of temperatures displaying substantial increase in this fraction also shows substantial temperature dependence of the average inherent structure energies.

Figure 6 shows the fraction of molecules with five or higher coordination. Complementary to the variation of the fraction of four coordinated molecules, this fraction approaches values very close to zero as  $T_c$  is approached.

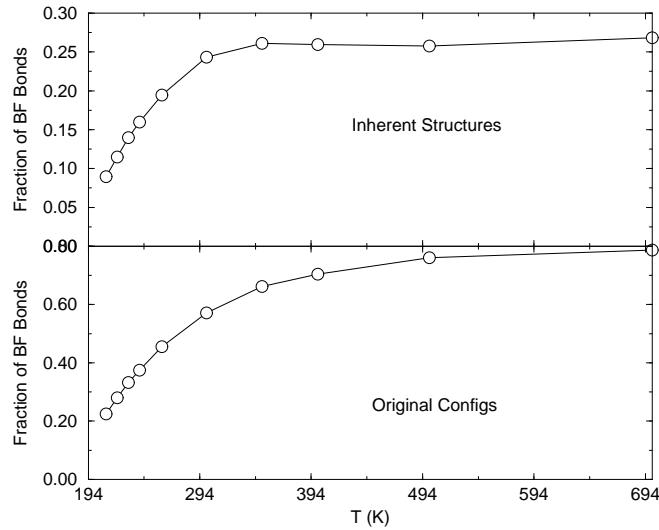


FIG. 6. Fraction of five or higher coordinated water molecules: (a) Equilibrated configurations, and (b) Inherent structures

#### IV. SUMMARY

We have presented simulation results that demonstrate the significant correlations between relaxation times, average energies of local potential energy minima sampled, and structural features for a simulation model of water. In particular, as the mode coupling temperature  $T_c$  estimated for this model liquid at the studied density is approached, the structure of the liquid appears to approach that of a four-coordinated network, free of defects to the extent permissible by the bulk density of the liquid. Such a structural change can potentially explain the speculated dramatic changes both in the dynamics and thermodynamic properties of water across this crossover temperature. Below the crossover temperature, no further structural arrangement may be expected, and the configurational entropy of the liquid may become ‘frozen in’ at the value that corresponds to the random tetrahedral network (plus the residual defects that may be present at concentrations varying with density). Thus

the rate of change in entropy of the liquid would change substantially near the crossover temperature. Similarly, because of the significant temperature dependence of the fraction of bifurcated bonds – which facilitate structural rearrangement – above the crossover temperature, and the relative constancy below, the temperature dependence of the dynamical properties may also be expected to show a corresponding crossover. Further work is in progress to strengthen these notions.

We acknowledge useful discussions with Prof. C. A. Angell. FS acknowledges INFM-PRA and MURST-PRIN, and HES acknowledges NSF, for financial support.

\* Email: sastry@jncasr.ac.in

- [1] O. Mishima, L. D. Calvert and E. Whalley, *Nature* **288**, 76 (1985).
- [2] C. A. Angell, in *Water: A Comprehensive Treatise*, F. Franks, ed. (Plenum Press, New York, 1972) vol. 7.
- [3] R. J. Speedy and C. A. Angell, *J. Chem. Phys.* **65**, 851 (1976).
- [4] P. H. Poole, F. Sciortino, U. Essmann and H. E. Stanley, *Nature* **360**, 324 (1992).
- [5] S. Sastry, P. G. Debenedetti, F. Sciortino and H. E. Stanley, *Phys. Rev. E* **53**, 6144 (1996).
- [6] F. Sciortino, P. Gallo, P. Tartaglia and S.-H. Chen, *Phys. Rev. E* **54**, 6331 (1996).
- [7] K. Ito, C. T. Moynihan and C. A. Angell, *Nature* **398**, 492 (1999); S. Sastry, *Nature* **398**, 467 (1999).
- [8] F. Starr, C. A. Angell, R. J. Speedy and H. E. Stanley, (preprint).
- [9] C. A. Angell, *J. Non-Cryst. Solids* **131-133**, 13 (1991).
- [10] F. Sciortino, A. Geiger, and H. E. Stanley, *Nature* **354**, 218 (1991).
- [11] R. S. Smith and B. D. Kay, *Nature* **398**, 788 (1999); K.P. Stevenson, G. A. Kimmel, Z. Dohnalek, R. S. Smith, and B. D. Kay, *Science* **283**, 1505 (1999).
- [12] S. Sastry, P. G. Debenedetti and F.H. Stillinger, *Nature* **393**, 554 (1998).
- [13] F. Sciortino, W. Kob and P. Tartaglia, *Phys. Rev. Lett.* **83**, 3214 (1997).
- [14] A. Scala, F. W. Starr, E. La Nave, F. Sciortino and H. E. Stanley, cond-mat/9908301.
- [15] L. Angelani, G. Parisi, G. Ruocco and G. Viliani, *Phys. Rev. Lett.* **81** 4648 (1998).
- [16] S. Buechner and A. Heuer, cond-mat/9906278; cond-mat/9906280.
- [17] C. J. Roberts, P. G. Debenedetti and F. H. Stillinger (preprint).
- [18] H. J. C. Berendsen, J. R. Grigera, and T. P. Stroatsma, *J. Phys. Chem.* **91**, 6269 (1987).
- [19] F.W. Starr, F. Sciortino, and H.E. Stanley, *Phys. Rev. E* **60**, 6757 (1999).
- [20] T. A. Weber and F. H. Stillinger, *J. Chem. Phys.* **87**, 3252 (1987).